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Plasma catalytic oxidation of methane on alumina-supported noble metal catalysts

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ABSTRACT

The methane oxidation reaction was studied as a function of temperature for a gas mixture representative of a combined heat power (CHP) within a dielectric barrier discharge (DBD) reactor. The effect of energy deposition was studied, with energy deposition ranging from 36 to 58 $J L^{-1}$, to maintain a low NO_x formation at high temperature. In the current study, we also investigated the combined process of a dielectric barrier discharge and γ-alumina noble metal catalysts such as platinum and palladium. In order to separate the catalytic effects from the plasma activation, the work included both purely catalytic and plasma activation processes using a complete CHP mixture with 4% of water in the feed. It was found that the presence of water leads to increase the methane conversion in purely plasma activation processes. Moreover, a higher efficiency for methane oxidation in CHP conditions was observed with the plasma–Pd(X)/Al_2O_3 systems.

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1. Introduction

The huge world-wide presence of natural gas, much larger than crude oil, in addition to the fact that natural gas combustion offers significant environmental advantages, makes it an attractive alternative to other energy sources (gasoline, diesel and coal). Although natural gas combustion provides several advantages, the emission of unburned methane, which is the main component of natural gas, is a drawback given that methane is a potent greenhouse gas, which is recognized to contribute more to global warming than CO_2 at equivalent emission rates. Moreover, its lifetime is quite long [1].

The total oxidation of methane raises numerous difficulties. Indeed, the high stability of the methane molecule together with the following reaction conditions: the low temperatures at which the catalyst must operate (less than 500–550 °C); the low concentrations of methane (500–1000 ppm); the large amounts of water vapour (10–15%) and CO_2 (15%); the large excess of oxygen, and the presence of SO_x (about 1 ppm) and NO_x (about 150 ppm) did not lead to an ideal catalyst which should exhibit the highest activity at the lowest temperature and the best resistance to poisons present in the exhaust gases.

Numerous studies have been performed to design catalytic materials that present the highest activity and the best resistance to poisons present in exhaust gases [1–9]. Noble metal catalysts such as oxide carriers supported-palladium and, to a lesser extent, supported-platinum, appeared as the best catalysts. Their properties in the complete oxidation of methane at low temperature were extensively studied so far [1,10]. Although being the most active, Pd catalysts exhibit a strong sensitivity to water- and sulfur-containing compounds, which represents serious drawbacks to their use for natural gas vehicles (NGV) or combined heat power (CHP) exhaust after treatment [1]. It was reported that water acts as a strong inhibitor to the catalytic activity in methane oxidation, by competing with methane for adsorption on catalytic sites [9,11–15].

Recently, Salmeron et al. [16] showed that during oxidation process palladium surface oxidation proceeds by a formation of stable and metastable structures. In addition, water would induce the progressive transformation of surface PdO active sites into $Pd(OH)_2$ less active sites [4,11,12,14,15,17] leading to an irreversible deactivation of the palladium-based catalysts. Sulfur-containing compounds were shown to readily convert into SO_x and strongly adsorb at the surface of PdO particles as stable sulfate species. These latter species lead to a complete loss of catalytic activity for methane oxidation [18–23]. Water could also increase the deactivation rate of Pd/Al_2O_3 catalysts for reaction temperatures of at least 400 °C [5,6]. Much fewer studies were devoted to Pt catalysts. It was shown that Pt would be more resistant to sulfur poisoning [1,18].

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An alternative to catalytic oxidation of methane may be the use of plasmas. In the last years various thermal and non-thermal plasmas, dielectric barrier discharge (DBD), corona, gliding arc, microwave, glow discharge and pulsed discharge, combining or not combining catalysts have been widely investigated. In plasmas gaseous species are chemical dissociated producing excited species (molecules and atoms) and activated particles (ions and radicals) by electron impact. Plasmas are a powerful technology for several applications, such as methane conversion into higher hydrocarbons [24–34], methane reforming [30,35–46], NO_x treatment [36,47–54] and abatement of VOC [55,56]. Most of the products produced using corona, microwave, and radio frequency discharges are small molecules, such as ethylene, acetylene, hydrogen and carbon monoxide. Complex products including light hydrocarbons, liquid fuels, alcohols and acids are often produced with a DBD [29].

Although the various studies were performed, plasma technology was not too much developed in a way to oxidize methane into CO_2 from emissions of combined heat powers. Only, recently, Hueso et al. used a microwave plasma technology to oxidize methane in excess of oxygen [52]. They studied the effect of the supports on methane oxidation. They showed that the plasma yields CO plus H_2O as majority products. However, a small extra oxidation to CO_2 is found at low temperature when a catalyst (SiO_2 or $La_{1-x}Sr_xCoO_{3-d}$ (x = 0.5) perovskite) is placed in the glow zone of the plasma. They claimed that with the perovskite, the oxidation efficiency to CO_2 increased with temperature up to 90% at 180 °C. In a previous study [57], we investigated the combined process of a dielectric barrier discharge and γ-alumina catalyst in the total oxidation of methane. It was found that the catalytic activity depended on the energy deposition and the temperature. The plasma process leads to methane conversion in the temperature range of 300–500 °C, whereas, methane conversion was only active above 425 °C when only a catalyst was present. Moreover, the addition of NO_x and CO_2 in the feed was also studied. This addition does not affect the methane conversion in the absence or in the presence of catalyst. Finally, the presence of γ-alumina leads to CO + CO_2 as products of the total oxidation of methane, whereas for the plasma-induced.

In this paper, we present the results of recent experiments using a dielectric barrier discharge for total methane oxidation. The aim of the present study is to investigate the catalytic activity of palladium- and platinum-supported γ-alumina catalysts in the complete oxidation of methane traces under lean conditions at low temperature, in presence of plasma DBD in using energy deposition of 36 or 58 J L^{-1}. A comparison of those systems was then reported in pointing out the effect of plasma. The effect of gas hourly space velocity was studied. Finally, the importance of water, present in the CHP exhaust gases, was also examined.

2. Experimental

2.1. Catalyst preparation

0.5 and 1.6 wt.% Pd (0.36 wt.% Pt) catalysts were prepared by impregnation of crushed and sieved γ-Al_2O_3 (0.8 mm < d < 1.2 mm) (Procatalyse, specific surface area of 190 $m^2 g^{-1}$, pore volume of 0.7 $cm^3 g^{-1}$ with $Pd(NH_3)_4(NO_3)_2$ ($Pt(NH_3)_4(NO_3)_2$) aqueous solution), the suspension being maintained under stirring at 333 K for 1 h. After complete removal of water by evaporation under reduced pressure, the catalysts were dried overnight in air at 393 K and calcined in air at 773 K for 4 h. The catalysts preparation procedure is well described elsewhere [15]. The as-prepared catalysts are labeled Pt(X)/Al_2O_3 or Pd(X)/Al_2O_3, in which X is the theoretical content of noble metal, and are presented in Table 1.

Table 1
Physico-chemical properties of platinum- and palladium-based catalysts

Samples	BET area ($m^2 g^{-1}$)	Metal content E.A. (wt.%)	PME (%)
γ-Al_2O_3	190	0	0
Pt(0.36)/Al_2O_3	179	0.36	20
Pd(0.5)/Al_2O_3	176	0.48	23
Pd(1.66)/Al_2O_3	174	1.66	21

2.2. Characterization of catalysts

The palladium and platinum catalysts, before and after reaction, were characterized by XRD, H_2–O_2 titration, transmission electron microscopy (TEM). The specific surface area was also measured using a home-made apparatus. Main physico-chemical properties of the catalysts are reported in Table 1.

Elemental analysis was performed by the "Service Central d'Analyses du CNRS" in order to determine the platinum and palladium contents. Powder X-ray diffraction (XRD) was carried out on a Siemens model D-500 diffractometer with Cu Kα radiation. High-resolution transmission electron microscopy (HRTEM) was performed to determine the particle size of platinum particles on alumina and to check their dispersion. HRTEM studies were performed on a JEOL-JEM 100 CXII apparatus associated with a top entry device and operating at 100 kV. The platinum and the palladium percentage of metal exposed (PME) measurements were carried out by hydrogen–oxygen titration using a conventional pulsed technique (Micromeritics). Insensitive structure reaction [58] was also used for the counting of $Pt^{(0)}$ species. It has shown that the number of exposed zero-valent Pt(0) atoms can be deduced from the turnover rate of benzene hydrogenation [58]. Benzene hydrogenation measurements were conducted in a conventional device described elsewhere [59,60]. In a typical run, prior to benzene hydrogenation, catalysts were pretreated at 400 °C in flowing hydrogen, then cooled to the temperature reaction under helium, and finally submitted to the H_2/C_6H_6 mixture.

2.3. Plasma–catalysis system

A schematic view of the DBD reactor presented Fig. 1 is well described elsewhere [57]. The reactor was a quartz tube with an

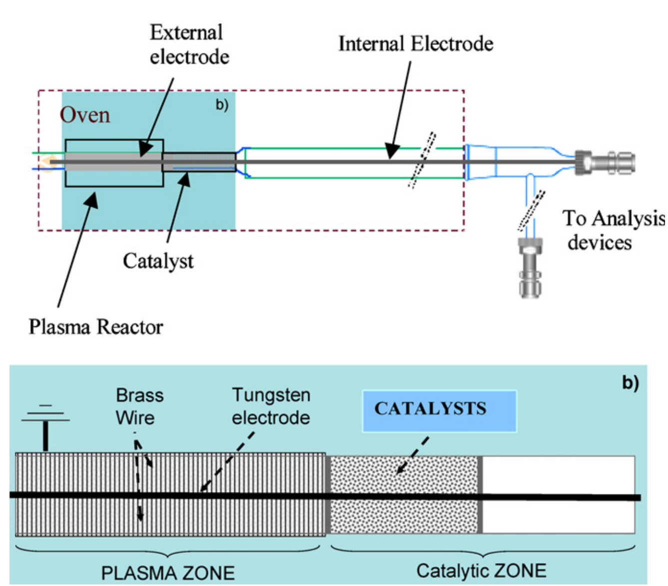

Fig. 1. Scheme of plasma catalytic system.

inner diameter of 12 mm, decomposed in two zones. The plasma was created in the first one and, in the second zone the catalyst could be placed, if necessary. The electrical discharge reactor is DBD. The reactor geometry was one of wire to cylinder type. It consisted of a tungsten wire (thickness, 0.9 mm) centered in a dielectric tube, and fixed with two ceramic rings. The outer surface of tube was coated with a brass wire to form the outer electrode. The length of the discharge zone was 150 mm, with a gap of 5.5 mm. To drive the discharge an ac high voltage was generated with a maximum of 14 kV. The frequency of applied voltage varied in the range of 25–40 kHz. The applied voltage and current were measured using a high voltage probe (TEKTRONIX P6015A, 1000×) and a current probe (EUROPULSE 9001), respectively [61]. The output signals were transmitted to a digitizing oscilloscope (TEKTRONIX 2440). The discharge pulse energy into the plasma was measured with a capacitive circuit. The energy deposition in the plasma reactor, $\mathrm{J\,L^{-1}}$ is given by $E_d = (E_p/Q)f$, in which, E_p is the discharge pulse energy (maintained at 14 kV), f the pulse repletion frequency, and Q is the gas flow rate at standard conditions (25 °C and 1 atm). In our conditions, the discharge pulse energy was maintained constant at about 35 mJ pulse^{-1}.

The catalyst, surrounded with quartz wool, was placed in the second zone of the reactor, close to the discharge zone. The length of the catalytic bed varied from 5 to 20 mm. The bed temperature was measured using a type K thermocouple affixed to the outer reactor surface. The temperature was controlled using an electronic controller (Eurotherm, 2408) and a resistively heated furnace (Eraly). The catalytic activity was measured at atmospheric pressure in the same DBD plasma quartz reactor.

2.4. Catalytic studies

In order to investigate the methane total oxidation, two different reaction mixtures were considered. The reactants are the following: 150 ppm NO, 8% O_2, 7% CO_2, 1000 ppm CH_4, 0% H_2O in N_2 as balance; 150 ppm NO, 8% O_2, 1000 ppm CH_4, 7% CO_2, 4% H_2O in N_2 as balance, respectively. The NO mixture was supplied by Air Liquide as 0.1% NO and 99.9% N_2 (<10 ppm other gases). The O_2 mixture contained 4.99% O_2 and 95.01% N_2 (Air Liquide). The CH_4 mixture contained 1% CH_4 and 99% N_2 (Air Liquide). The CO_2 mixture contained 100% CO_2. The total gas flow was maintained at 0.25 L min^{-1} NTP. Each of the gas mixtures was metered using calibrated electronic mass flow controllers (Brooks, Model 5850E).

The reactor outflow was analyzed using a set of specific detectors. An Eco Physics CLD 700 AL NO_x Chemiluminescence's analyzer (for NO and total NO_x (*i.e.* $NO + NO_2$)) allowed the simultaneous detection of NO, NO_2 and NO_x. An Ultramat 6 IR analyzer was used to monitor N_2O and a FID detector was used to follow the total concentration of hydrocarbons (HC). GC–MS analyses were performed on-line using an AGILENT device (GC 6890-MS 5973 N) equipped with a CP-PoraBOND Q capillary column (Chrompack, 30 m long, 0.32 mm inner diameter, 0.5 μm film thicknesses) with temperature programming from 50 to 280 °C. NIST spectral AGILENT database was used to identify the detected products. The methane concentration was followed by gas micro-chromatography (Agilent G2890A). This apparatus allowed also the analysis of various gases such as H_2, O_2, N_2, CO, and CO_2, in a scale ranging from ppm to %. The analysis time is lower than 120 s.

Steady-state activity, methane conversion, was measured in the presence or in absence of catalyst at different temperatures, ranging from 300 to 500 °C. The methane conversion was defined as follows:

$$\text{methane conversion}\,(\%) = \frac{\text{moles of methane consumed}}{\text{moles of methane introduced}} \times 100$$

For each methane conversion, for example 10%, the corresponding temperature was denoted T_{10}. These latter temperatures were compared to discuss about the efficiency of plasma conditions or catalytic activity.

3. Results and discussion

3.1. Effect of catalyst composition on the methane oxidation in CHP conditions, in absence of water

The experimental conditions were presented in Table 2 as function of the catalysts. The total flow rate was maintained constant at 250 mL min^{-1}. The space velocity GHSV was varied from 20,000 to 400,000 h^{-1} depending on the catalyst, to have a significant activity. Alumina-supported palladium- and platinum-based catalysts have been used in this study. For both catalysts, no particles have been detected by the characterization techniques, leading to the conclusion that the active phase was well dispersed on the support. Indeed, by TEM or XRD, only alumina patterns (JCPDS 10-0425) have been detected. Moreover, the percentage of the number of exposed zero-valent Pt(0) atoms (PME) was deduced from the turnover rate of benzene hydrogenation [58]. The PME for different catalysts are reported in Table 1. Finally, the specific surface was measured for each catalyst. The specific surface area decreases from 190 to 174 m^2 g^{-1} upon the impregnation of active phases. This slight variation indicates that the alumina is only affected by the impregnation of metal and that eventual changes in the catalytic properties for methane oxidation could not originate from surface transformations of the alumina support.

3.1.1. Palladium-based catalysts

Palladium-based catalysts are well known to be the most active catalysts for the catalytic total oxidation of methane [1]. A catalyst, Pd(1.66)/Al_2O_3, was tested in presence and in absence of an energy deposition of 36 J L^{-1}, under the following reaction mixture: 150 ppm NO, 8% O_2, 7% CO_2, 1000 ppm CH_4, 0% H_2O in N_2 as balance, with a GHSV of 20,000 h^{-1}. The results are presented in Fig. 2. According to the literature [1,14,15], in absence of water, the methane is converted in CO_2 above 250 °C.

In presence of plasma alone, *i.e. in absence of catalyst*, the methane is only activated from 300 °C [57], the conversion depending on the energy deposition. Thus, at 300 °C, the methane is almost totally converted in presence of catalyst alone.

In these conditions, the effect of plasma is not evident. Due to the high activity of catalyst around 300 °C, one can see in Fig. 2, that the effect of plasma is not significant in presence of Pd(1.66)/Al_2O_3. In addition, the energy deposition was increased from 36 to 58 J L^{-1} to improve the activity of the plasma-assisted reaction. The methane conversion is unchanged from 36 to 58 J L^{-1}, in presence of Pd(1.66)/Al_2O_3 catalyst (Fig. 2). Indeed, we have shown elsewhere that the influence of energy deposition was not evident

Table 2
Experimental conditions for methane oxidation

Catalyst	Catalyst weight ($\times 10^{-3}$ g)	Total flow (mL min^{-1})	GHSV (h^{-1})
γ-Al_2O_3	270	250	40,000
Pd(0.5)/Al_2O_3	270	250	40,000
Pd(1.66)/Al_2O_3	540	250	20,000
	28	250	400,000
Pt(0.36)/Al_2O_3	108	250	100,000
	540	250	20,000

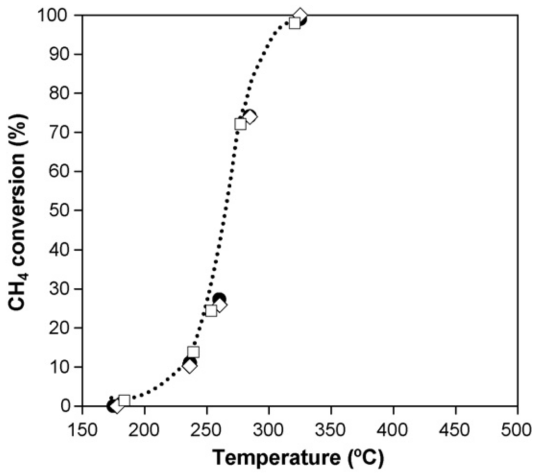

Fig. 2. CH_4 conversion as function of temperature in presence of Pd(1.66)/Al_2O_3 (GHSV = 20,000 h^{-1}, 540 mg) in absence of energy deposition (●); with an energy deposition equal to 36 J L^{-1} (◇); with an energy deposition equal to 58 J L^{-1} (□).

at low temperature (300 °C), the effect of energy deposition was only clearly evident at high temperature (above 450 °C) [57]. Thus, a new experiment has been performed to show the influence of plasma on the methane oxidation. The same experimental conditions were considered, only the GHSV was changed to 400,000 h^{-1} (25 mg of catalyst). The results are presented in Table 3. In these new experimental conditions, 50% of methane is converted at 340 °C for E_d = 0, 36 and 58 J L^{-1}. In comparison, with a GHSV = 20,000 h^{-1}, 50% conversion was obtained at 275 °C for E_d = 0, 36 and 58 J L^{-1}. Again, there is no influence of plasma (energy deposition) in presence of Pd(1.66)/Al_2O_3. Finally, the palladium content was decreased and new experiments were performed with a Pd(0.5)/Al_2O_3 with a GHSV = 40,000 h^{-1} to minimize the influence of catalyst in the catalytic plasma-assisted system (Table 3). Then, 50% of methane is converted at 330 °C for E_d = 0, 36 and 58 J L^{-1}. Again, there is no influence of the energy deposition in presence of Pd(0.5)/Al_2O_3. In the studied experimental conditions, the palladium-based catalysts are highly active in the temperature range from 350 to 500 °C (in which the plasma activates the methane). Thus, for palladium-based catalysts, there is no influence of plasma on the methane total oxidation. For all the experiments, only CO_2 was observed as product. No CO and by-products of methane were detected. Moreover, we can note that in the operating conditions only ca. 20 ppm of NO_x were formed at 500 °C whereas 100% methane is converted (E_d = 36 J L^{-1}).

3.1.2. Platinum-based catalysts

A platinum-based catalyst, Pt(0.36)/Al_2O_3, has been prepared and has been studied under the following reaction mixture: 150 ppm NO, 8% O_2, 7% CO_2, 1000 ppm CH_4, 0% H_2O in N_2 as balance, with a GHSV of 20,000 h^{-1}. The reaction of methane oxidation was carried out in the absence of plasma and in presence of an energy deposition ranging from 36 to 58 J L^{-1}. The results are presented in Fig. 3. One can see, that in absence of plasma, the Pt(0.36)/Al_2O_3 catalyst oxidized the methane above 350 °C, with a significant conversion of 45% at 475 °C. These results are in agreement with the literature [1]. Indeed, the platinum-based catalysts are less active than palladium ones for methane total oxidation in absence of water [1,15].

In presence of an energy deposition (36 and 58 J L^{-1}), the methane conversion increases with the energy deposition. In Fig. 3, one can see that 10% of methane is converted at 420, 338 and 325 °C for E_d = 0, 36 and 58 J L^{-1}, respectively and 30% of methane

Table 3
Temperature of n% methane conversion, T_n, under different energy deposition, in presence of different catalysts

Catalyst	GHSV (h^{-1})	Energy deposition (J L^{-1})	n% methane conversion temperature (°C)		
			T_{30}	T_{50}	T_{80}
–	–	36	430	470	–
–	–	58	410	450	
Pd(1.66)/Al_2O_3	20,000	0	255	275	285
		36	255	275	285
		58	255	275	285
Pd(1.66)/Al_2O_3	400,000	0	322	340	397
		36	322	340	397
		58	322	340	397
Pd(0.5)/Al_2O_3	40,000	0	315	330	362
		36	315	330	362
		58	315	330	362
Pt(0.36)/Al_2O_3	100,000	0	–	–	–
		36	422	460	–
		58	395	438	485
Pt(0.36)/Al_2O_3	20,000	0	462	–	–
		36	412	448	–
		58	388	426	462
From Ref. [59] (Al_2O_3)	20,000	0	470	–	–
		36	412	448	–
		58	398	435	470

is converted at 460, 412 and 388 °C for E_d = 0, 36 and 58 J L^{-1}, respectively. Thus, the influence of plasma is clearly evident in presence of a platinum-based catalyst. The catalytic plasma-assisted system is then efficient for energy deposition ranging from 36 to 58 J L^{-1} and alumina-supported catalysts. In presence of platinum only CO_2 was observed as product for methane oxidation. Again, no CO and by-products of methane were detected, and a low amount of NO_x is formed at 500 °C (ca. 30 ppm for E_d = 58 J L^{-1}).

3.1.3. Comparison between the different catalytic active phases

Table 3 summarizes the experiments that have been carried out in absence of water.

As we already discussed above for the plasma–Pd(X)/Al_2O_3 system, due to the high reactivity of palladium, there is no influence of energy deposition. However, in presence of plasma–Pt(X)/Al_2O_3

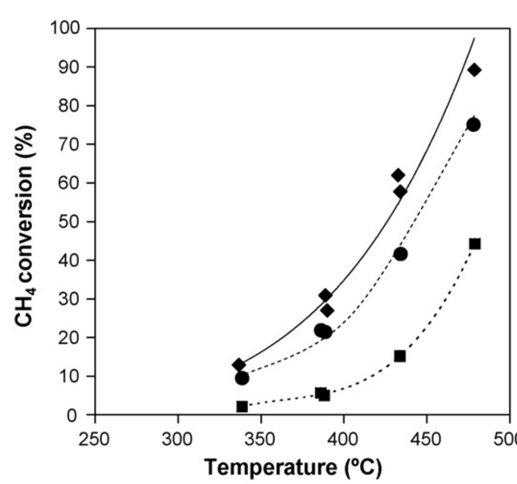

Fig. 3. Effect of energy deposition (J L^{-1}) on the CH_4 conversion as function of temperature ((□) 0 J L^{-1}, (●) 36 J L^{-1} and (◆) 58 J L^{-1}), in absence of water, over Pt/Al_2O_3 (GHSV = 20,000 h^{-1}, 540 mg) 150 ppm NO, 8% O_2, 7% CO_2, 1000 ppm CH_4 in N_2 as balance.

system, there is clearly an influence of energy deposition, the methane conversion varying with the energy deposition.

Indeed, in Table 3, a comparison with the support alone was performed at GHSV = 20,000 h^{-1}. On alumina alone, 30% of conversion is obtained at 470, 412 and 398 °C for E_d = 0, 36 and 58 J L^{-1}, respectively and 30% of methane is converted at 462, 412 and 388 °C for E_d = 0, 36 and 58 J L^{-1}, respectively on Pt(0.36)/Al_2O_3; and 30% of methane is converted at 255 °C whatever the energy deposition was 0 or 58 J L^{-1}, respectively on Pd(1.66)/Al_2O_3. An energy deposition influence is then evident on plasma–catalytic system composed with alumina alone or with Pt(0.36)/Al_2O_3. For 30% methane conversion in absence of plasma, the reaction temperature is 50 °C higher, in comparison with a plasma–Pt(0.36)/Al_2O_3 system with E_d = 36 J L^{-1}. The reaction temperature reaches up to 75 °C for higher energy deposition.

In these operating conditions, Pd catalysts exhibit a superior catalytic activity in methane oxidation compared to Pt ones, whatever the catalysts contained low or high metal content. Moreover, the platinum activity is not significant for the methane oxidation, in comparison to support alone.

In absence of water the plasma–Pd(X)/Al_2O_3 system is as efficient as Pd(X)/Al_2O_3 alone; there is no influence of plasma on methane oxidation. However, at high temperature (400–500 °C) with a plasma–Pt(X)/Al_2O_3 system or plasma–Al_2O_3 system, the influence of energy deposition is clearly evident, leading a decrease of about 50 °C of the reaction temperature depending on the energy deposition.

3.2. Influence of water on the methane oxidation in CHP conditions, using a plasma system

The experiments were carried out for the following gas mixture: 150 ppm NO, 8% O_2, 1000 ppm CH_4, 7% CO_2 and 4% H_2O in N_2 as balance.

3.2.1. Effect of water on methane conversion in absence of catalyst as function of energy deposition

The influence of water on the methane oxidation in presence of plasma DBD was studied as function of energy deposition in gas phase reaction. Two energy depositions were chosen, 36 and 58 J L^{-1}. The results are presented in Fig. 4a and b. Using 36 J L^{-1}, the oxidation of methane is enhanced in the presence of wet feed only at high temperature (above 400 °C). Indeed, at 450 °C, 40% of methane oxidation is achieved in absence of water whereas 48% is converted in presence of water. On the contrary, with higher energy deposition (58 J L^{-1}), the influence of water is evident since 350 °C. At this temperature the methane conversion is about 10% in dry feed and 20% in wet feed. Moreover, at 450 °C, about 50% of methane is converted in absence of water whereas about 65% is converted in presence of water. The presence of water increased the total oxidation of methane by promoting the CO_2 formation. It could be due to the high affinity of water to electrons, in presence of energy deposition. Indeed, in presence of plasma the following reaction (1) takes place [61,62]:

$$e^- + H_2O \rightarrow e^- + H^\bullet + OH^\bullet \qquad (1)$$

This finding suggested that water could affect not only discharge property but also reactions enhanced by discharge. Since water contributes the formation of $H^\bullet$ and $OH^\bullet$ radicals [61,62], CO_2 formation is possibly accelerated by $H^\bullet$ and $OH^\bullet$ related.

These results agreed with previous studies conducted using high-frequency pulsed plasma for oxidizing methane and activated carbon powder as two substitutes for diesel particulate matter (PM) [63]. Yao et al. [63] have shown that the presence of water

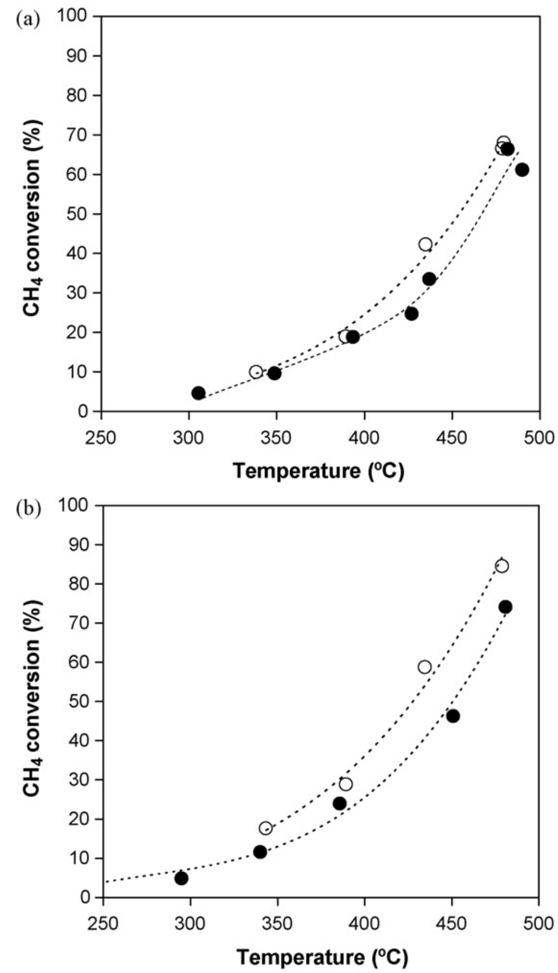

Fig. 4. Effect of H_2O concentration in the feed on the CH_4 conversion in absence of catalyst (*gas phase reactions*) (○) with H_2O and (●) without H_2O. (a) Energy deposition = 36 J L^{-1}. (b) Energy deposition = 58 J L^{-1}.

decreased the partial oxidation under the same experimental condition due to the high affinity of water to electrons, but increased CO_2 formation. The influence of water has been also studied for NO_x reduction using plasma systems in absence of hydrocarbons [64] or in presence of hydrocarbons [65–67]. According to Fujii et al. [64], ozone and the $OH^\bullet$ radicals produced in corona discharge space are important to promote the oxidation reactions. In the reactor with water, abundant humidity and $OH^\bullet$ radicals enhance the following reactions:

$$O^\bullet + H_2O \rightarrow 2OH^\bullet \qquad (2)$$

$$NO_2 + OH^\bullet \rightarrow HNO_3 \qquad (3)$$

In addition, the corona wind toward water surface helps to dissolve NO_2, previously created by the oxidation of NO by ozone, into water. In presence of hydrocarbons, Park et al. [65] and Ravi et al. [66] have found the NO removal efficiency in presence of water in the feed was higher in the all range of studied temperature. Both authors proposed that the plasma reactor releases $OH^\bullet$ radicals (reaction (1)) which in turn oxidize NO to NO_2 through the following reactions:

$$NO + OH^\bullet \rightarrow HNO_2 \qquad (4)$$

$$HNO_2 + OH^\bullet \rightarrow NO_2 + H_2O \qquad (5)$$

In our conditions, even at high temperatures, in presence of water the amount of NO_x formed is not significant.

Moreover, Park et al. [65] have calculated the reaction rate in absence of water – only in presence $O^\bullet$ radicals – and in wet feed, in presence of $OH^\bullet$ radicals. The authors have found that in presence of water, as function of used hydrocarbons, the rate could be one order of magnitude higher than those obtained in dry conditions.

For a sake of comparison and to avoid any effect of CO_2, runs in absence of CO_2 were performed. The experiments led to similar results. No effect of CO_2 was observed in our operating conditions. No $CO_2 + CH_4$ reaction was observed.

3.3. Influence of water on the methane oxidation in CHP conditions, for a coupled plasma–catalytic system

Figs. 5–7 present the results of methane oxidation in presence of water as function of energy deposition and as function of catalyst.

3.3.1. Influence of wet mixture on support

The activity of alumina-based catalysts for the methane oxidation was presented elsewhere [57]. In presence of water the methane oxidation was totally inhibited. The alumina alone was inactive in the studied range of temperature. The one effect observed was the effect of energy deposition, as already reported in dry conditions [57].

3.3.2. Influence of water on platinum- and palladium-based catalysts

Since numerous authors mentioned a strong inhibition of water vapour on the rate of methane oxidation, which could be responsible for the observed deactivation of Pd catalysts [9,12,14–16,68], we decided to confirm the effect of water on the noble metal-based catalysts in CHP conditions. Figs. 5a, 6a, and 7a present the activity of different noble metal catalysts in absence and in presence of water for $E_d = 0\ J\ L^{-1}$. As already reported in the literature [9,12,14–16,68], the methane oxidation rate decrease with the addition of water in the feed. Indeed, on Pt(0.36)/Al_2O_3, 10% of methane conversion is obtained at 425 and 475 °C, for $E_d = 0\ J\ L^{-1}$, in dry and in wet conditions, respectively. In addition, on Pd(1.66)/Al_2O_3 (GHSV = 400,000 h^{-1}), 50% of methane is converted at 405 and 455 °C, in dry and in wet conditions, respectively. Finally, 50% of methane is converted at 340 °C in absence of water and at 385 °C in presence of water on Pd(0.5)/Al_2O_3 (GHSV = 40,000 h^{-1}).

The loss of activity on water addition was then consistent with previous studies on Pd/Al_2O_3 indicating the strong inhibition by water vapour [5,9,13–16,68]. Van Giezen et al. [9] and Ribeiro et al. [13] have measured a negative order with respect to water vapour pressure. These negative orders in water concentration could be related to a competitive adsorption of methane and water on the active site. More recently, Roth et al. [14] have showed that small amounts of water vapour inhibited the oxidation of methane, which was in contradiction with the results of Cullis and Willatt [17] for which the inhibition only took place at relatively large water concentrations and was negligible at low water concentrations. Moreover, it is generally agreed that Pd is present in the form of PdO at relatively low temperatures and under lean conditions. Indeed, Farrauto et al. have shown that the formation of Pd metal phase led to a decrease of the methane oxidation activity and that the reoxidation of metallic phase induced the recovery of the activity [24]. In presence of water, Burch et al. have then reported the possible formation of surface $Pd(OH)_2$, less active than PdO and stabilised by alumina [12,17]. As reported Gélin's group [14,15], if oxide ions are required to activate methane C–H bond, it is clear that the rate of the oxidation reaction will depend on the rate of dehydroxylation of the surface to recreate surface oxide sites. Hydroxyls formed at the PdO surface might be expected to slowly diffuse to sublayers of PdO phase and form $Pd(OH)_2$ domains more difficult to dehydroxylate and reform PdO surface sites, thus explaining the slow catalyst deactivation.

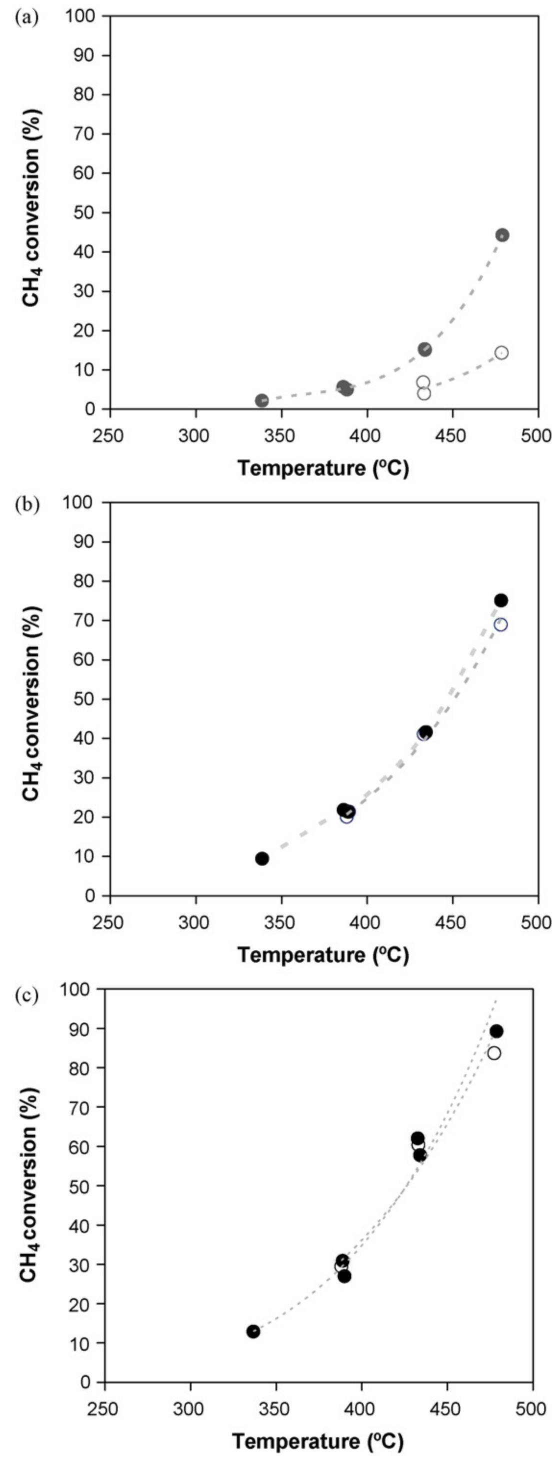

Fig. 5. Effect of H_2O in the feed on the CH_4 conversion as function of temperature in presence of Pt(0.36)/Al_2O_3 ((GHSV = 20,000 h^{-1}, 540 mg); 150 ppm NO, 8% O_2, 7% CO_2, 1000 ppm CH_4 in N_2 as balance) (○) with H_2O and (●) without H_2O. (a) Energy deposition = 0 J L^{-1}. (b) Energy deposition = 36 J L^{-1}. (c) Energy deposition = 58 J L^{-1}.

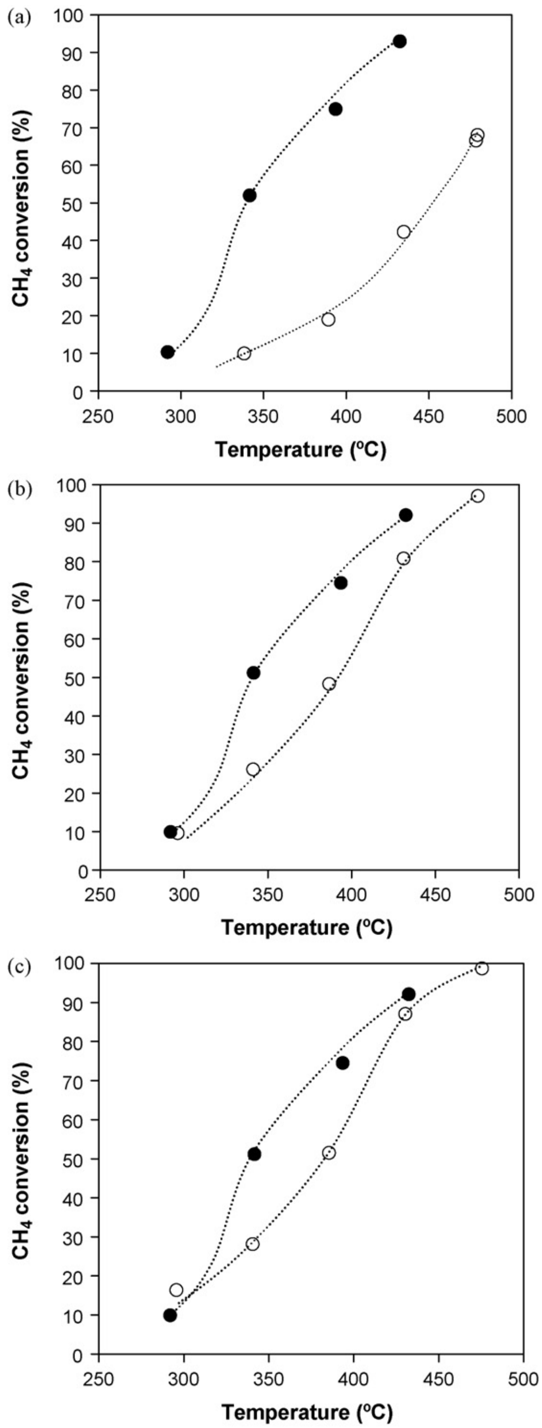

Fig. 6. Effect of H_2O in the feed on the CH_4 conversion as function of temperature in presence of Pd(1.66)/Al_2O_3 ((GHSV = 400,000 h^{-1}, 28 mg); 150 ppm NO, 8% O_2, 7% CO_2, 1000 ppm CH_4 in N_2 as balance) (○) with H_2O and (●) without H_2O. (a) Energy deposition = 0 J L^{-1}. (b) Energy deposition = 36 J L^{-1}. (c) Energy deposition = 58 J L^{-1}.

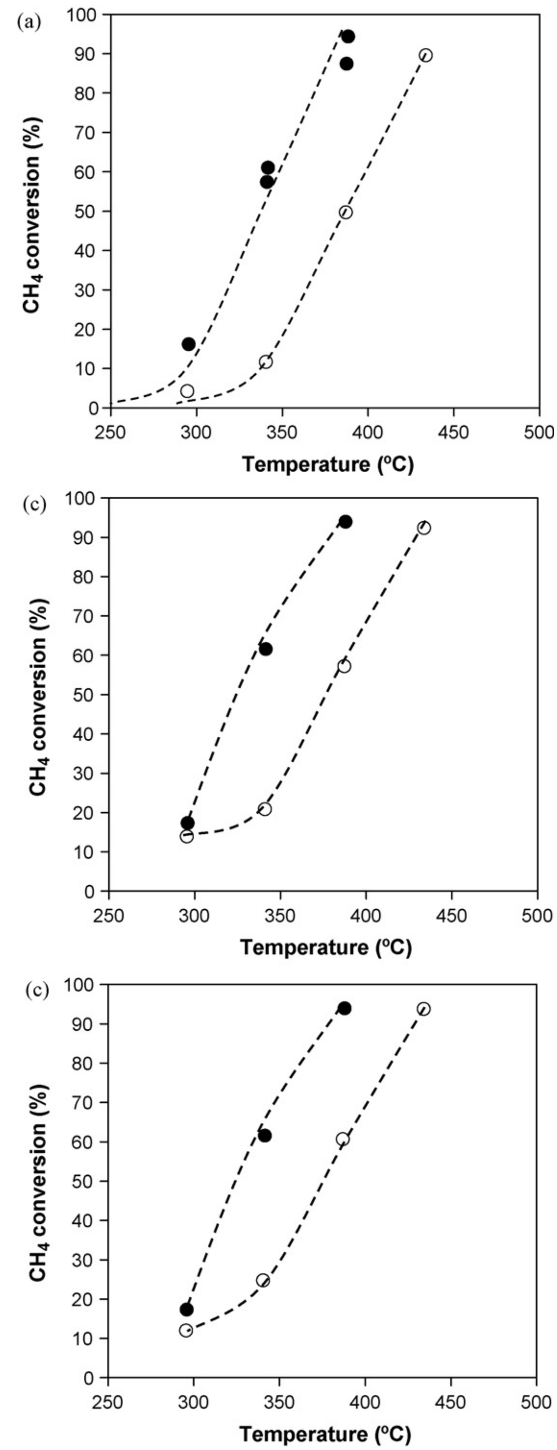

Fig. 7. Effect of H_2O in the feed on the CH_4 conversion as function of temperature in presence of Pd(0.5)/Al_2O_3 ((GHSV = 40,000 h^{-1}, 270 mg); 150 ppm NO, 8% O_2, 7% CO_2, 1000 ppm CH_4 in N_2 as balance) (○) with H_2O and (●) without H_2O. (a) Energy deposition = 0 J L^{-1}. (b) Energy deposition = 36 J L^{-1}. (c) Energy deposition = 58 J L^{-1}.

3.3.3. Coupled plasma–Pt(X)/Al_2O_3 or plasma–Pd(X)/Al_2O_3 for methane oxidation in presence of water in the feed

Two energy deposition were studied, 36 and 58 J L^{-1}. The results for platinum-based catalysts are reported in Fig. 5b and c. As already reported in absence of plasma (Fig. 5a), the platinum catalyst is inactive for methane conversion in presence of water. With a plasma addition, one can conclude the same. In fact, in Fig. 5b and c, for E_d = 36 and 58 J L^{-1}, whatever the experimental conditions, 50% of methane is converted at the same temperature, 450 and 430 °C, respectively. The enhancement of methane oxidation is only due to the increase of energy deposition, as already reported [57]. We can then conclude that systems with plasma DBD coupled with platinum-based catalysts are not efficient system for methane oxidation in wet exhaust conditions.

On the contrary, a difference of reactivity is observed on plasma coupled with palladium-based catalysts in presence of water (Figs. 6b and c and 7b and c). One can see that over Pd(1.66)/Al_2O_3 (GHSV = 400,000 h^{-1}) and for E_d = 36 J L^{-1}, 50% of methane is converted at 345 °C in absence of water and at 390 °C in presence of water (Fig. 6b and c). The same conclusion can be drawn from Pd(0.5)/Al_2O_3 (Fig. 7b and c). Again, as already reported in absence of plasma and in literature [5,9,13–16,68], a loss of activity was observed in presence of water.

However, for plasma–palladium systems, the influence of energy deposition becomes significant. Indeed, in comparison to catalytic systems alone, an increase of activity is observed in wet conditions, whereas no significant synergetic effect was observed in dry conditions. For Pd(1.66)/Al_2O_3 (GHSV = 400,000 h^{-1}), 50% of methane is converted at 455, 390 and 385 °C for E_d = 0, 36 and 58 J L^{-1}, respectively. For Pd(0.5)/Al_2O_3 (GHSV = 40,000 h^{-1}), 50% of methane conversion is obtained at 390, 375 and 370 °C for E_d = 0, 36 and 58 J L^{-1}, respectively. For both palladium catalysts, in wet conditions, the methane conversion increases with increasing the energy deposition.

The negative effect of water on palladium catalysts, which can be explained by adsorption competition [9,13] or by the change of active phase [12,14,15,17] is partially drawn aside by the positive effect of water on plasma systems, which generates $OH^{\bullet}$ radicals accelerating the CO_2 formation [61,62]. In wet CHP conditions, the most efficient system for methane oxidation is the plasma + Pd(X)/Al_2O_3 system.

4. Conclusions

Plasma–catalytic processes are promising processes to treat exhaust gases such as methane, NO_x or VOC [36,47–56]. Only few studies dealt with plasma catalytic methane oxidation [52,57]. In this study, the methane oxidation reaction was studied in CHP experimental conditions using catalytic systems such as palladium or platinum catalysts; using plasma DBD alone with energy deposition ranging from 36 to 58 J L^{-1}; or using plasma and catalysts systems.

In absence of water, palladium catalysts exhibit a superior catalytic activity in methane oxidation compared to Pt ones, whatever the catalysts contained low or high metal content. Moreover, the platinum activity is not significant for the methane oxidation, in comparison to support alone.

Furthermore, the plasma–alumina-supported palladium system is as efficient as Pd(X)/Al_2O_3 alone. There is then no influence of plasma on methane oxidation for these systems, in absence of water.

However, at high temperature (400–500 °C) with a plasma–Pt(X)/Al_2O_3 system or plasma–Al_2O_3 system, the influence of energy deposition is clearly evident, leading a decrease of about 50 °C of the reaction temperature depending on the energy deposition. In absence of water, the presence plasma is not needed and the most efficient system is based on Pd(X)/Al_2O_3 catalysts.

In presence of water in the feed, the methane oxidation rate decrease with the addition of water in the feed. Indeed, on noble metal-based catalysts, the same methane conversion is obtained at temperatures 50 °C higher in wet conditions in comparison to dry mixtures. The loss of activity on water addition was then consistent with previous studies on Pd/Al_2O_3 indicating a strong inhibition by water vapour and a modification of surface active phase PdO. In the same experimental conditions, the platinum-based catalysts are inactive.

For DBD plasma alone, it was found that methane oxidation rate increases with the water addition and with energy deposition. Indeed, the presence of water creates with plasma $OH^{\bullet}$ radicals, which leads to higher rate of methane oxidation to CO_2. At 450 °C, with 36 J L^{-1}, 50% of methane oxidation is achieved. This effect is even more evident if the E_d is increased.

Finally, plasma–catalysts systems were studied in wet conditions. In presence of plasma, the methane oxidation rate observed for plasma–Pt(X)/Al_2O_3 system only corresponds to the influence of energy deposition. Indeed, the presence of water creates $OH^{\bullet}$ radicals, which leads to higher rate of methane oxidation.

Moreover, in presence of plasma, for both palladium catalysts, in wet conditions, the rate of methane conversion is enhanced significantly compared to catalytic system alone. In these latter experiments, the negative effect of water on palladium catalysts is partially drawn aside by the positive effect of water on plasma systems.

In wet CHP conditions, the most efficient system for methane oxidation is the plasma–Pd(X)/Al_2O_3 system, depending on the desired reaction temperature. These coupled plasma/catalysis systems could be a good alternative to decrease the amount of noble metal in the methane oxidation reaction and more generally in hydrocarbon oxidation processes.

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